

## PREDICTION OF KINETICS FOR C<sub>4</sub> SPECIES WHICH FORM BENZENE

Phillip R. Westmoreland

Chemical Engineering Department  
University of Massachusetts - Amherst  
Amherst, Massachusetts 01003

### INTRODUCTION

C<sub>4</sub> species have long been proposed to be critical intermediates in forming aromatics from lighter aliphatics. Recent work (1) supports the hypotheses that 1-buten-3-ynyl (1-C<sub>4</sub>H<sub>3</sub>) and 1,3-butadienyl (1-C<sub>4</sub>H<sub>5</sub>) are the specific species involved in low-pressure flames of acetylene (C<sub>2</sub>H<sub>2</sub>) and 1,3-butadiene (1,3-C<sub>4</sub>H<sub>6</sub>).

1-C<sub>4</sub>H<sub>3</sub> and 1-C<sub>4</sub>H<sub>5</sub> have been suggested before as the key reactants (2-6), but the recent work shows that the earlier, thermal mechanisms are not justified; rather, only chemically activated pathways are feasible. Earlier studies generally assumed addition to C<sub>2</sub>H<sub>2</sub>, followed by thermal cyclization of the linear adduct to phenyl and cyclohexadienyl, respectively, and by thermal decomposition of the cyclohexadienyl to benzene and H. All reactions were implicitly assumed to be in the high-pressure limit. However, appropriate analysis of falloff indicates that this thermal sequence is too slow, even at 1 atm, while chemically activated intermediates from the same addition reactions lead directly to aromatics with fast enough rate constants.

Identifying the sources of 1-C<sub>4</sub>H<sub>3</sub> and 1-C<sub>4</sub>H<sub>5</sub> is plainly of interest. Literature analyses (2-6) assumed these sources were addition of C<sub>2</sub>H and C<sub>2</sub>H<sub>3</sub> to C<sub>2</sub>H<sub>2</sub>, again (implicitly) in the high-pressure limit. Also, the quantitative test in (1) was comparison of the measured, net rate of benzene formation to a rate calculated from predicted rate constants and the measured C<sub>2</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>3</sub>, and C<sub>4</sub>H<sub>5</sub> concentrations. An improved test would use concentrations of the specific isomers 1-C<sub>4</sub>H<sub>3</sub> and 1-C<sub>4</sub>H<sub>5</sub>, which could not be resolved from other C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> isomers experimentally.

Rates are predicted and compared here for the reactions that form and destroy 1-C<sub>4</sub>H<sub>3</sub>, 1-C<sub>4</sub>H<sub>5</sub>, and other C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> isomers. Rate constants are estimated by analogy and thermochemical kinetics (7) for H-abstraction from 3-butenyne (C<sub>4</sub>H<sub>4</sub> or vinylacetylene) and from 1,3-C<sub>4</sub>H<sub>6</sub>. Using Bimolecular Quantum-RRK (8-9), rate constants, branching and pressure dependence are predicted for the association reactions of radical addition (C<sub>2</sub>H+C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>3</sub>+C<sub>2</sub>H<sub>2</sub>), H-addition (to C<sub>4</sub>H<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>), and H/radical and radical/radical recombination (H+C<sub>4</sub> radicals, C<sub>2</sub>H+C<sub>2</sub>H<sub>3</sub> and C<sub>2</sub>H<sub>3</sub>+C<sub>2</sub>H<sub>3</sub>).

## EXPERIMENTAL AND THEORETICAL PROCEDURES

Experimental data. - Profiles of mole fractions were mapped for 38 stable species and free radicals in a lightly sooting flat flame of  $\text{C}_2\text{H}_2/\text{O}_2/5\% \text{ Ar}$  (10) using molecular-beam mass spectrometry. The fuel-equivalence ratio was 2.40, burner velocity (298 K) was 0.50 m/s, and pressure was 2.67 kPa (20 torr). Temperatures were measured using a 0.076-mm diameter Pt/Pt-13%Rh thermocouple, coated with a thin  $\text{BeO}/\text{Y}_2\text{O}_3$  glass to eliminate catalytic heating and resistively heated to the flame temperature so as to eliminate convective heat transfer. Mole fractions were shifted 0.11 mm toward the burner (two orifice diameters), compensating for the shift caused by the probe.

Direct and indirect calibrations were used, and the smoothed data curves were used in the present calculations. Major stable species were calibrated directly within 3% except for  $\text{H}_2\text{O}$  (25%). Minor species were calibrated within a factor of two by the method of relative ionization cross-sections (11). Because of the correction for  $^{13}\text{C}$  isotope effects and the low signals, the shapes of the radical profiles are less well defined than those of the minor stable species.

Complete profiles for all species of interest except  $\text{C}_2\text{H}$  and  $\text{O}$  were measured. For  $\text{C}_2\text{H}$  and  $\text{O}$ -atom in the present calculations, mole fractions were predicted (10) using a modified Warnatz (12-13) reaction mechanism.

Predicted rate constants. - Two types of reactions were considered: abstractions of  $\text{H}$  and association reactions, which include additions, combinations, and (by microscopic reversibility) unimolecular decompositions. Abstraction rate constants and high-pressure-limit association rate constants may be estimated by simple analogies or by more complex analogies such as thermochemical kinetics. However, as noted above, proper consideration of pressure effects is necessary for association reactions. Even at 1 atm and for relatively large molecules, these effects can be significant at combustion temperatures (14).

Bimolecular Quantum-RRK (8-9) was used here to predict falloff for addition and combination reactions. The method also predicts rate constants for the chemically activated decomposition paths, which numbered as many as three in the present study. These rate constants are also influenced by pressure but have an inverse falloff behavior (pressure-independent at low pressures (9)). Input data needed for the method are high-pressure-limit, Arrhenius pre-exponential factors and activation energies for each association and dissociation step; geometric mean frequency and number of frequencies in each adduct; and collisional properties of adduct and bath molecules.

Arrhenius parameters  $A$  and  $E_{\text{act}}$  were estimated for one direction of reaction, and the parameters for the reverse reaction then were calculated using the equilibrium constant (microscopic reversibility). For example, rate constants

for radical combinations were estimated by an extension (10) of a method of Benson (15) and were assumed independent of temperature.

#### ESTIMATION OF THERMODYNAMICS AND OF RATE CONSTANTS

Species involved in the reactions to be analyzed include H, H<sub>2</sub>, O, OH, H<sub>2</sub>O, C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>4</sub> (vinylacetylene), 1,2,3-C<sub>4</sub>H<sub>4</sub> (butatriene), 1,3-C<sub>4</sub>H<sub>6</sub>, and the C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> radicals. Few data are available for the thermodynamics and kinetics of C<sub>4</sub> species. The necessary data may be estimated with useful accuracy, but data uncertainties and their effects must be examined.

Thermodynamics. - These properties (Table 1) were estimated using group additivity. The groups of Benson (7) were supplemented by the recent groups for unsaturates and rings by Stein and Fahr (16). Additional groups for vinyl (ethenyl) and ethynyl radical sites were derived from the heats of formation (298 K) of 70.4 kcal/mol for C<sub>2</sub>H<sub>3</sub> (17) and 135 kcal/mol for C<sub>2</sub>H (inferred from (18)). These values appear reliable, but other values as low as 63 and 127 have been suggested.

Structural assignments must be made in order to apply group additivity to the C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> radicals. For 1-C<sub>4</sub>H<sub>3</sub> or 1-C<sub>4</sub>H<sub>5</sub>, the radical site is on a terminal alkene carbon, and properties are inferred by analogy of 1-C<sub>4</sub>H<sub>3</sub>/C<sub>4</sub>H<sub>4</sub> or 1-C<sub>4</sub>H<sub>5</sub>/1,3-C<sub>4</sub>H<sub>6</sub> with C<sub>2</sub>H<sub>3</sub>/C<sub>2</sub>H<sub>4</sub>. Similarly, properties of the CH<sub>2</sub>CHCC· radical can be estimated from C<sub>4</sub>H<sub>4</sub> and C<sub>2</sub>H/C<sub>2</sub>H<sub>2</sub>, and for HCC-CH=CH·, from 1-butyne and C<sub>2</sub>H<sub>3</sub>/C<sub>2</sub>H<sub>4</sub>. Even for HCC-CH·-CH<sub>3</sub>, the species is easily treated as an allylic radical of 1-butyne.

The remaining two radicals, HCC-C·=CH<sub>2</sub> (2-C<sub>4</sub>H<sub>3</sub>) and CH<sub>2</sub>=CH-C·=CH<sub>2</sub> (2-C<sub>4</sub>H<sub>5</sub>), are more difficult. No groups are available for vinylic radical sites like these that are created inside conjugated pi-bond systems. Instead, thermodynamics are estimated for equivalent resonance structures for 2-C<sub>4</sub>H<sub>3</sub> and 2-C<sub>4</sub>H<sub>5</sub>, respectively ·CH=C=C=CH<sub>2</sub> and ·CH<sub>2</sub>-CH=C=CH<sub>2</sub>. The first, allenic radical is assumed to be formed with the 110 kcal/mol bond dissociation energy of C<sub>2</sub>H<sub>4</sub>, while the second radical is treated as a simple allylic site.

The properties are summarized in Table 1. In addition, necessary geometric-mean frequencies were estimated from frequency assignments and are included in Table 1. Rougher estimates could have been used, as the quantized energy distribution is not affected greatly.

Table 1. Estimated thermodynamic properties and geometric-mean frequencies (enthalpy in kcal/mol; entropy in cal/mol K).

	$\Delta H_f, 298$ S298		Cp (cal/mol K) at T (K)=										$\langle \omega \rangle$ , cm <sup>-1</sup>
			300K	400	500	600	800	1000	1500	2000			
C <sub>2</sub> H	135.0	49.6	8.9	9.7	10.2	10.7	11.5	12.2	13.3	14.1			
C <sub>2</sub> H <sub>3</sub>	70.4	54.5	10.9	12.4	13.8	15.1	17.2	18.8	21.3	23.2			
C <sub>4</sub> H <sub>2</sub> (HCC-CCH)	105.1	59.8	17.6	20.1	21.9	23.2	25.1	26.6	29.1	30.5			
1-C <sub>4</sub> H <sub>3</sub> (HCC-CH=CH.)	126.1	66.5	17.2	20.1	22.4	24.4	27.2	29.2	32.7	34.4	1000		
2-C <sub>4</sub> H <sub>3</sub> (HCC-C'=CH <sub>2</sub> )	138.7	68.3	17.5	20.2	22.5	24.4	27.4	29.6	33.2	34.7	1040		
CH <sub>2</sub> =CH-CC'	149.2	65.3	15.8	18.8	21.4	23.5	26.9	29.3	33.0	34.4			
C <sub>4</sub> H <sub>4</sub> (vinylacetylene)	68.2	65.1	17.5	21.2	24.2	26.6	30.3	33.1	37.6	39.7	1080		
123-C <sub>4</sub> H <sub>4</sub> (butatriene)	80.9	63.1	18.0	21.5	24.4	26.9	30.7	33.5	37.7	39.5			
1-C <sub>4</sub> H <sub>5</sub> (CH <sub>2</sub> =CH-CH=CH')	84.2	68.7	18.6	23.3	26.8	29.5	33.6	36.5	41.4	44.1	1140		
2-C <sub>4</sub> H <sub>5</sub> (CH <sub>2</sub> =CH-C'=CH <sub>2</sub> )	72.2	69.9	18.5	22.9	26.5	29.4	34.0	37.4	42.5	44.6	1160		
HCC-CH <sub>2</sub> -CH <sub>2</sub> '	85.6	70.7	19.4	23.3	26.5	29.3	33.5	36.7	42.6	46.2	1450		
HCC-CH'-CH <sub>3</sub>	96.6	73.1	18.8	22.4	25.5	28.3	32.7	36.1	41.5	43.9	1530		
1,3-C <sub>4</sub> H <sub>6</sub> (butadiene)	26.3	66.6	19.0	24.3	28.5	31.8	36.9	40.5	46.3	49.9	1190		
1-butyne	39.6	69.6	19.5	23.9	27.7	30.9	36.1	40.0	47.1	51.7			
2-butyne	35.0	68.2	18.7	22.7	26.4	29.7	35.2	39.3	45.5	49.2			

**Radical additions.** - Additions of C<sub>2</sub>H and C<sub>2</sub>H<sub>3</sub> to acetylene are the routes to 1-C<sub>4</sub>H<sub>3</sub> and 1-C<sub>4</sub>H<sub>5</sub> that have been assumed in previous analyses (2-6). One reason is that such addition leads only to an end radical on the C<sub>4</sub> adduct. Less recognized is that the adduct is initially rovibrationally excited (chemically activated) by the depth of the potential well where the ground-state adduct is located. Falloff can occur, and chemically activated decomposition of the hot adduct is possible to form H+C<sub>4</sub>H<sub>2</sub> or H+C<sub>4</sub>H<sub>4</sub>. Thus, 1-C<sub>4</sub>H<sub>3</sub> and H+C<sub>4</sub>H<sub>2</sub> are not different types of C<sub>2</sub>H+C<sub>2</sub>H<sub>2</sub> reactions but different product channels from the same addition.

Calculation shows that the decomposition channels dominate over the simple additions for both these reactions over the range of 900 to 2000 K at 2.67 kPa CO. Even at 1 atm N<sub>2</sub>, H+C<sub>4</sub>H<sub>2</sub> is faster than the 1-C<sub>4</sub>H<sub>3</sub> channel by a factor of 3 or more. For C<sub>2</sub>H<sub>3</sub>+C<sub>2</sub>H<sub>2</sub> at 1 atm N<sub>2</sub>, the addition/stabilization channel to 1-C<sub>4</sub>H<sub>5</sub> is faster than addition/decomposition to H+C<sub>4</sub>H<sub>4</sub> up to 1350 K, but the 1-C<sub>4</sub>H<sub>5</sub> channel has fallen off to 1% of the high-pressure limit at 2000 K.

**H-atom additions.** - Addition of H to C<sub>4</sub>H<sub>2</sub> or C<sub>4</sub>H<sub>4</sub> also can form C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> radicals. In this case, the H can add (in principle) to any carbon, giving different isomers, and some chemically activated decompositions of the adducts may occur.

H-addition to the end carbons of C<sub>4</sub>H<sub>2</sub> forms (2-C<sub>4</sub>H<sub>3</sub>)\*, which can only be stabilized if 1,3-H shifts are disallowed. Addition to the internal carbons forms 1-C<sub>4</sub>H<sub>3</sub> and C<sub>2</sub>H+C<sub>2</sub>H<sub>2</sub>' in the reverse of the radical addition sequence described above. Calculation shows that falloff makes the 2-C<sub>4</sub>H<sub>3</sub> product of H+C<sub>4</sub>H<sub>2</sub>

negligible, as the rate constants (2.67 kPa, 1500 K) are  $2.6 \cdot 10^{11}$ ,  $1.1 \cdot 10^{11}$ , and  $1.6 \cdot 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for 1-C<sub>4</sub>H<sub>3</sub>, C<sub>2</sub>H+C<sub>2</sub>H<sub>2</sub>, and 2-C<sub>4</sub>H<sub>3</sub>. C<sub>2</sub>H+C<sub>2</sub>H<sub>2</sub> begins to dominate at 1600 K for 2.67 kPa, but 1-C<sub>4</sub>H<sub>3</sub> remains dominant even at 2000 K at 1 atm.

The product spectrum from H+C<sub>4</sub>H<sub>4</sub> is more complex because addition to each different carbon gives a different adduct. Of the additions forming (1-C<sub>4</sub>H<sub>5</sub>)\* and (2-C<sub>4</sub>H<sub>5</sub>)\*, C<sub>2</sub>H<sub>3</sub>+C<sub>2</sub>H<sub>2</sub> dominates at 1500 K and 2.67 kPa ( $2.2 \cdot 10^{12}$ ), followed by 1-C<sub>4</sub>H<sub>5</sub> ( $7 \cdot 10^{11}$ ), 2-C<sub>4</sub>H<sub>5</sub> ( $2.5 \cdot 10^{11}$ ), and H+butatriene ( $6 \cdot 10^{10}$ ). Addition/stabilization to 1-C<sub>4</sub>H<sub>5</sub> is dominant at 1 atm to 1900 K. Here, as for radical addition, C<sub>4</sub>H<sub>5</sub> formation is less inhibited by falloff than is C<sub>4</sub>H<sub>3</sub> formation.

Radical/radical and H/radical combinations. - Combination reactions have not generally been considered as paths to C<sub>4</sub> radicals. However, chemically activated decompositions to H+C<sub>4</sub>H<sub>x</sub> are possible from C<sub>2</sub>H<sub>3</sub> combinations with C<sub>2</sub>H, forming (C<sub>4</sub>H<sub>4</sub>)\*, and with itself, forming (C<sub>4</sub>H<sub>6</sub>)\*. Combinations of H with C<sub>4</sub>H<sub>x</sub> radicals are also of interest as sinks and as reactive-isomerization reactions for the radicals.

Formation of 1-C<sub>4</sub>H<sub>3</sub> +H is dominant at 2.67 kPa for both C<sub>2</sub>H+C<sub>2</sub>H<sub>3</sub> and for 2-C<sub>4</sub>H<sub>3</sub> +H reactions. Thermalized C<sub>4</sub>H<sub>4</sub> is the only other significant product from 2-C<sub>4</sub>H<sub>3</sub> +H, while C<sub>2</sub>H+C<sub>2</sub>H<sub>3</sub> forms minor amounts of C<sub>4</sub>H<sub>4</sub> and 2-C<sub>4</sub>H<sub>3</sub> +H. From the reaction of 1-C<sub>4</sub>H<sub>3</sub> +H, formation of C<sub>4</sub>H<sub>4</sub> is strongly favored at both pressures.

In contrast, C<sub>2</sub>H<sub>3</sub>+C<sub>2</sub>H<sub>3</sub> leads predominantly to thermalized 1,3-C<sub>4</sub>H<sub>6</sub>. The 2-C<sub>4</sub>H<sub>5</sub> +H and 1-C<sub>4</sub>H<sub>5</sub> +H channels are within an order of magnitude of the C<sub>4</sub>H<sub>6</sub> channel at 1500 K and 2.67 kPa, but C<sub>4</sub>H<sub>6</sub> formation is even more strongly favored at 1 atm. Both C<sub>4</sub>H<sub>5</sub>+H channels are similarly dominated by C<sub>4</sub>H<sub>6</sub> formation.

Thermal decompositions. - Thermal elimination of H by beta-scission can be an important loss mechanism for radicals. Thermal decompositions of molecules require more thermal activation and are usually not important in flames. In both cases, the kinetics may be calculated from unimolecular reaction theory, using the parameters developed for cases above, or from microscopic reversibility, using the rate constants developed above. In summary, elimination of H proved to be the dominant channel for the radicals, while formation of H + 1-C<sub>4</sub>H<sub>3</sub> or 1-C<sub>4</sub>H<sub>5</sub> was most important for decomposition of the molecules.

Application to flame data. - Only a few reactions prove to be important in determining the totals of formation and destruction rates. The above rate constants were combined with measured concentrations and temperature profiles to establish the dominant production and destruction channels of 1-

---

C<sub>4</sub>H<sub>3</sub>, 2-C<sub>4</sub>H<sub>3</sub>, 1-C<sub>4</sub>H<sub>5</sub>, and 2-C<sub>4</sub>H<sub>5</sub>. Rates were calculated as a function of position and also were integrated over distance.

1-C<sub>4</sub>H<sub>3</sub>, the apparent precursor of phenyl, is formed two orders of magnitude faster than 2-C<sub>4</sub>H<sub>3</sub>. This difference would give super-equilibrium concentrations of 1-C<sub>4</sub>H<sub>3</sub> because equilibrium levels of 2-C<sub>4</sub>H<sub>3</sub> should exceed 1-C<sub>4</sub>H<sub>3</sub>. Formation of 1-C<sub>4</sub>H<sub>3</sub> is primarily by H atom reactions with C<sub>4</sub>H<sub>2</sub> (addition) and with C<sub>4</sub>H<sub>4</sub> (abstraction), while destruction is dominated by loss of H to form C<sub>4</sub>H<sub>2</sub>.

One puzzle is that the integrated amount of destruction should be less than or equal to the integrated rate of formation. However, the predicted destruction is greater by a factor of 20. One possible reason is error in the C<sub>4</sub>H<sub>3</sub> calibration, as the destruction rate is proportional to C<sub>4</sub>H<sub>3</sub> concentration, while formation is independent of it. An alternative is that some formation reaction is not considered. C<sub>2</sub>H<sub>2</sub>+C<sub>2</sub>H<sub>2</sub> was examined using a literature rate constant (19) but it was three orders of magnitude too slow to make any difference.

1-C<sub>4</sub>H<sub>5</sub> was formed only at 45% of the rate of 2-C<sub>4</sub>H<sub>5</sub>, in contrast to the C<sub>4</sub>H<sub>3</sub> isomers. For both isomers, hydrogen abstraction by H was the principal source, with H+C<sub>4</sub>H<sub>4</sub> (addition) and thermal decomposition of 1,3-C<sub>4</sub>H<sub>6</sub> making up 1/10 to 1/3 of the total rate. Simple addition to form 1-C<sub>4</sub>H<sub>5</sub> was important only very early in the flame. This mix is illustrated in Figure 1. Total destruction was higher than formation for C<sub>4</sub>H<sub>5</sub>'s by a factor of ten. Again, either calibration error or a missing source reaction are suggested as reasons for this difference.

## CONCLUSIONS

Formation of 1-C<sub>4</sub>H<sub>3</sub> and 1-C<sub>4</sub>H<sub>5</sub> radicals is dominated by H-abstraction and H-addition. In contrast, previous workers had assumed that addition of C<sub>2</sub>H and C<sub>2</sub>H<sub>3</sub> to C<sub>2</sub>H<sub>2</sub> were responsible. This conclusion is qualified by the excessive destruction that is predicted, but calibration error may be the cause. Detailed experimental data, combined with careful, comprehensive theoretical predictions of rate constants, account for this new understanding.

This study is continuing, further examining the rate constants and using them in predictive flame mechanisms.

## ACKNOWLEDGEMENTS

Support of this C<sub>4</sub> study by the University of Massachusetts is gratefully acknowledged. The interest and insights of Professor Jack B. Howard, Professor John P. Longwell, and Dr. Anthony M. Dean are also appreciated.

## REFERENCES

1. Westmoreland, P. R., A. M. Dean, J. B. Howard, and J. P. Longwell, submitted for publication.
2. Kinney, R. E., and D. J. Crowley, *Ind. Eng. Chem.*, **46**, 258 (1954).
3. Stehling, F. C., J. D. Frazee, and R. C. Anderson, *Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 247, 1956.
4. Cole, J. A., J. D. Bittner, J. B. Howard, and J. P. Longwell, *Combustion and Flame*, **56**, 51 (1984).
5. Frenklach, M., D. W. Clary, W. C. Gardiner, Jr., and S. E. Stein, *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 887, 1984.
6. Frenklach, M., D. W. Clary, T. Yuan, W. C. Gardiner, Jr., and S. E. Stein, *Combust. Sci. and Tech.*, **50**, 79 (1986).
7. Benson, S. W., *Thermochemical Kinetics*, 2nd Ed., Wiley, 1976.
8. Dean, A. M., *J. Phys. Chem.*, **89**, 4600 (1985).
9. Westmoreland, P. R., J. B. Howard, J. P. Longwell, and A. M. Dean, *AIChE J.*, **32**, 1971 (1986).
10. Westmoreland, P. R., *Experimental and Theoretical Analysis of Oxidation and Growth Chemistry in a Fuel-Rich Acetylene Flame*, Ph. D. thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, 1986.
11. Lazzara, C. P., J. C. Biordi, and J. F. Papp, *Combustion and Flame*, **21**, 371 (1973).
12. Warnatz, J., *Combustion Science and Technology*, **34**, 177 (1983).
13. Westmoreland, P. R., J. B. Howard, and J. P. Longwell, *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, in press.
14. Golden, D. M., and C. W. Larson, *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 595, 1984.
15. Benson, S. W., *Can. J. Chem.*, **61**, 881 (1983).
16. Stein, S. E., and A. Fahr, *J. Phys. Chem.*, **89**, 3714 (1985).
17. McMillen, D. F., and D. M. Golden, *Ann. Rev. Phys. Chem.*, **33**, 493 (1982).
18. Wodtke, A. M., and Y. T. Lee, *J. Phys. Chem.*, **89**, 4722 (1985).
19. Tanzawa, T., and W. C. Gardiner, Jr., *J. Phys. Chem.*, **84**, 236 (1980).

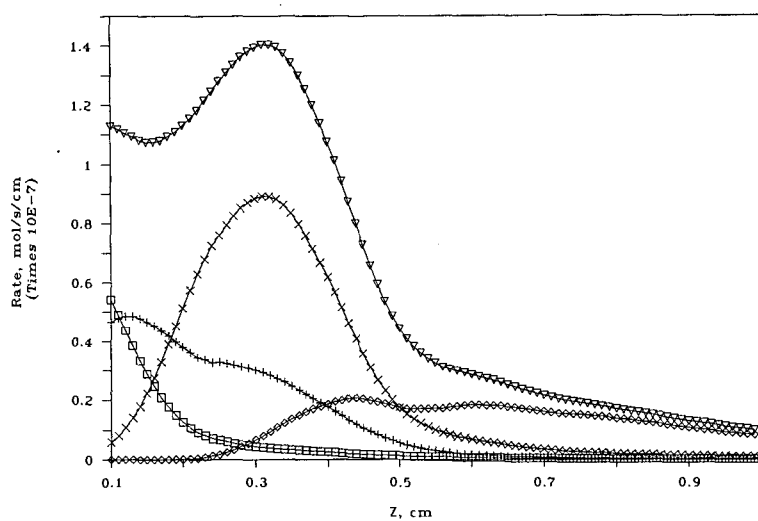


Figure 1. Predicted rates for reactions leading to 1-C<sub>4</sub>H<sub>5</sub>, using measured concentrations and predicted rate constants for C<sub>2</sub>H<sub>3</sub>+C<sub>2</sub>H<sub>2</sub> (□), H+C<sub>4</sub>H<sub>4</sub> (+), 1,3-C<sub>4</sub>H<sub>6</sub> decomposition (◇), 1,3-C<sub>4</sub>H<sub>6</sub> + H (×), and total (▽).